### V. *Observations on other Wave-lengths.*

A cursory examination was made of the structure of other lines in the spectrum of lithium, and it was found that the wave-length $\lambda = 6103{\cdot}77$ A. consisted of at least three well defined components. It was found difficult to make accurate visual observations as regards the wave-length $\lambda = 4602{\cdot}37$ A., but it was definitely seen to be resolved and consequently it had as a minimum two components. Detailed results of the measurements being made on these wave-lengths will appear in a later communication.

We desire to express our indebtedness to Mr. J. F. T. Young for calculations on the dispersion of the Lummer plate used in the experiments, and to Miss Cale and Mr. P. Blackman for assistance in preparing the illustrations in this paper.

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# *Interfacial Tension and Hydrogen-Ion Concentration.*

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(From the Physiological and Biochemical Laboratories, Cambridge.)

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## Section 1.—INTRODUCTION.

The predominance of hydrogen-ion concentration (1) in the colloidal chemistry of the proteins and other substances (Loeb (2)) makes imperative an investigation of those changes at the interface between two phases which are brought about by changes in hydrogen-ion concentration. Previous investigators have directed their attentions to the purely chemical aspects of the interfacial tension between soap solutions and oils, or to non-reactive chemical substances, such as benzene. Using a drop-weight method of measuring interfacial tension, Donnan (3) showed that crude rape oil and crude olive oil showed a much smaller interfacial tension against alkaline solutions (NaOH and Na carbonate) than against distilled water. The same olive oil showed no such difference against N/1000 NaOH after a process of purification, which was intended to remove the fatty acid. He also found that a paraffin showed no difference for interfacial tension when N/100 NaOH was substituted for distilled water, whereas the same paraffin containing 0·6 per cent. stearic acid, showed a large decrease when in contact with the alkaline solution. The decrease in interfacial tension, so produced, was found to be a function both of the amount of fatty acid dissolved in the paraffin, and also of the amount of alkali. It was further shown that of the series of acids, formic, acetic, butyric, caprylic, lauric, and stearic, tried respectively in solution in the paraffin, stearic and lauric acids alone showed any appreciable lowering of surface tension when an alkaline aqueous fluid was substituted for distilled water.

Harkins and Humphrey (4) extended Donnan's work by showing that alkali ($NH_4OH$) lowered the interfacial tension of benzene solutions of butyric and acetic acid against water. The depression of interfacial tension so produced was a function of the concentration of fatty acid, but tended to become maximal for butyric acid at a concentration of 0·5 mols. per litre. Later, Clowes (5) showed that the decrease in interfacial tension produced by alkalis, such as Na, K, Li, at the interface crude olive oil-water, was lessened by the presence of divalent salts, such as Ca and Ba.

### *Methods and Technique.*

Early in this research we used a capillary height method. For this was substituted a more reliable drop-weight technique. Some measurements were also made by a ripple method.

*Drop-weight Method.*—A 1 c.c. graduated pipette was turned round at the lower end. The turned-up end was ground as flat as possible. (In some experiments a pipette has been used with turned-down tip, *i.e.*, the aqueous phase has been dropped into the oil.) It was then attached to a small piston, fitted with a screw at its upper end. By turning the screw it was thus possible to fill the pipette with the liquid to be tested, and also to control very accurately the quantity of liquid delivered during the formation of single drops.

All apparatus used in connection with the work was carefully cleaned using for the most part boiling *aqua regia*, with a preliminary treatment with alcoholic potash if necessary.

The buffer solutions used (namely, phthalate, phosphate, and borate) were 0·05 M concentration of these constituents, as described by Clark and Lubs (6).

The hydrogen-ion concentration required in a given case is obtained by adding soda. The term "buffer" is here used in the physiological sense to denote a fluid in which the hydrogen-ion concentration has been stabilised by the addition of the salt of a weak acid.

The buffer solutions were put into glass weighing bottles of convenient size which were then placed side by side in a beaker of water, which acted as a convenient water bath. Some of the liquid under investigation was poured upon the top of the acid buffer. The pipette was lowered into the liquid to be investigated, and some of the fluid drawn up into it as far as the zero mark. The pipette was then lowered, so that its nozzle was completely immersed in the buffer solution, and a small amount of buffer solution drawn into the end of it so as to wet the tip. This was a necessary precaution, since the drops should come from the inner edge of the tip and not the outer, as the liquids used did not wet the glass.

The readings given for the drop volume are the average of several determinations. Care has been made to render the readings as far as possible comparative. In all cases the drop was finally allowed to break away slowly. As has been pointed out by many observers, the drop values for the most viscid fluids, like triolein, require a considerable time for attainment of equilibrium. The average error in the reading of the pipette was approximately 0·002 c.c. Where 0·5 c.c. of fluid has been run out, the total error upon the reading might amount to 1 per cent. The average of three readings should reduce the error considerably.

The values for the interfacial tension have been calculated, using as a basis the values for the interfacial tension of water-benzene, which have been found by careful measurement by Harkins and Humphrey (4) to be 34·98 dynes at 10° C. and 34·52 dynes at 20° C.* Equation (1) was used for calculating the interfacial tension $T_{AB}$.

(See Hardy)
$$T_{AB} = \frac{b\,(D_B - D_A)\,g}{nrf}. \tag{1}$$

Here,
$b$ = volume of drop in cubic centimetre,
$D_B$ = density of aqueous layer,
$D_A$ = density of benzene,
$g$ = gravity (981),
$r$ = radius of tube,
$f$ is an empirical factor,
$n$ = number of drops (taken as 1).

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* We are aware that the use of benzene for calibration is open to criticism, but do not consider that it affects the comparative accuracy of our results. Two different bore pipettes calibrated in the above manner gave almost identical results.

*rf* was found by direct determination of the drop volume for the benzene water interfaces for this apparatus. Table I shows the calculation of the constant.

Table I.

| Temperature. | Volume, 1 drop. | $D_B$. | $D_A$. | $T_{AB}$. | *rf*. |
|---|---|---|---|---|---|
| 9·7° C. | 0·06355 | 0·9998 | 0·8918 | 34·99 | 19·24 |
| 20·7° C. | 0·05717 | 0·9981 | 0·8781 | 34·49 | 19·51 |

Interpolated values of *rf* have been used in calculating the results.

Some of our observations have also been confirmed by the ripple method, first applied practically by Rayleigh (7). This is fully described later.

### *Temperature.*

Experiments have been made at room temperature, and the interfacial tensions have been calculated for the temperature of the experiment without attempt to reduce to a common standard. Temperature variations in interfacial tension have been shown to be small.

### *Purification of Olive Oil.*

Two empirical methods have been used for the purification of olive oil in these experiments. (1) The crude olive oil has been boiled for 12 to 36 hours with frequent changes of tap water and then allowed to cool. (2) The oil has been purified by fractional crystallisation at −5° C.

## Section 2.—THE RELATIONSHIP BETWEEN HYDROGEN-ION CONCENTRATION AND INTERFACIAL TENSION.

Measurements of the interfacial tension between purified olive oil and aqueous fluids of various $P_H$* performed with the drop-weight method showed that there is a gradual fall in drop weight as the aqueous phase becomes more alkaline.

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* The "Sorensen" notation is used throughout to express hydrogen-ion concentration ($C_H$):—

$$pH = -\log C_H, \text{ i.e., if } C_H = 10^{-2}, \; pH = 2.$$

Table II.—Aqueous Phase dropped into Oil.

| P.H. | Buffered fluid. | Drop volume. | Interfacial tension in dynes per cm. |
|---|---|---|---|
| 3·0 | Phosphate | 0·117 | 14·7 |
| 4·0 | Phosphate | 0·117 | 14·7 |
| 4·4 | Phthalate | 0·118 | 14·8 |
| 5·0 | Phosphate | 0·112 | 14·1 |
| 5·6 | Phosphate | 0·092 | 12·5 |
| 6·0 | Phosphate | 0·088 | 11·9 |
| 6·4 | Phosphate | 0·082 | 10·7 |
| 6·4 | Borate | 0·082 | 10·9 |
| 7·0 | Phosphate | 0·072 | 9·6 |
| 7·0 | Borate | 0·076 | 10·1 |
| 7·6 | Phosphate | 0·059 | 7·7 |
| 7·6 | Borate | 0·058 | 7·7 |
| 8·0 | Phosphate | 0·047 | 6·1 |
| 8·0 | Borate | 0·045 | 5·9 |
| 8·6 | Phosphate | 0·027 | 3·4 |
| 8·6 | Borate | 0·026 | 3·4 |
| 9·2 | Borate | (Unmeasurable) | (Unmeasurable) |

A similar result is also obtained if the capillary height method of measurement be employed.

Table III.

| $P_H$. | Capillary height in mm. | | Interfacial tension in dynes per cm. |
|---|---|---|---|
| | Tube (*a*). | Tube (*b*). | |
| 4·0 | 51 | — | 13·5 |
| 5·0 | 49 | — | 13·0 |
| 6·0 | 46 | — | 12·2 |
| 6·6 | — | 31 | 11·7 |
| 6·8 | — | 29 | 11·0 |
| 7·0 | 37 | 26 | (9·8) |
| 7·2 | — | 24 | 9·1 |
| 7·4 | — | 23 | 8·7 |
| 7·6 | — | 22 | 8·3 |
| 8·0 | 28 | — | 7·4 |
| 9·0 | 9 | — | 2·4 |

And the two different methods of measurement give confirmatory results as shown in fig. 1.

It was not conclusively shown, however, that the change in drop weight and capillary height was actually produced by a change in the interfacial tension since in both methods the glass forms a third phase which may introduce effects due to angle of contact.

A method was, therefore, developed which was not liable to such effects, viz., the ripple method,* first applied practically by Rayleigh (7). This observer measured by its means the surface tension of water under various conditions. Dorsey (8) improved the technique and determined the surface tension of various aqueous solutions. Watson (9) has used the method for determining the interfacial tension of various organic liquids against mercury. The principal difficulty met with is connected with the measurement of the waves, because when the two liquids are of nearly the same refractive index the intensity of the light reflected from the interface is small. For this and other reasons the method was reconsidered, and the following alterations in the design of the apparatus were effected.

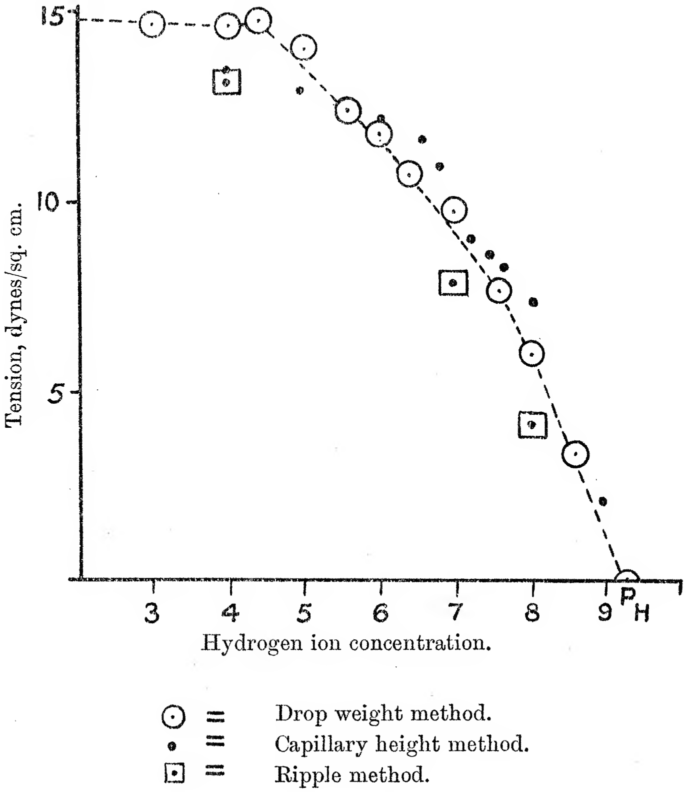

Fig. 1.

(1) The transmitted beam is measured in preference to the reflected beam. The three observers mentioned above made their measurements in the light reflected from the top surface of fluid or mercury as the case might be.

(2) In the original apparatus two synchronous electrically-driven tuning-forks were used, one for creating the waves and the other for rendering the beam of light intermittent. These were replaced by a motor-driven shaft,

which operated a system of levers for setting up the waves and also a rotating sector for rendering the light intermittent. The diagram (fig. 2) below gives a general view of the apparatus.

The beam of light, having passed through the condenser and interrupter, was rendered parallel by the collimators, and was then directed down on the surface of the liquids by means of the mirrors. These beams were refracted at the interface between the liquids by the waves, which act like weak cylindrical lenses, so that lines of light are formed on the bottom of the trough. Each of these lines corresponded to the crest of one of the waves, and, therefore, by measuring the distance between the lines by a suitable millimetre scale the wave-length of the ripples at the interface is ascertained.

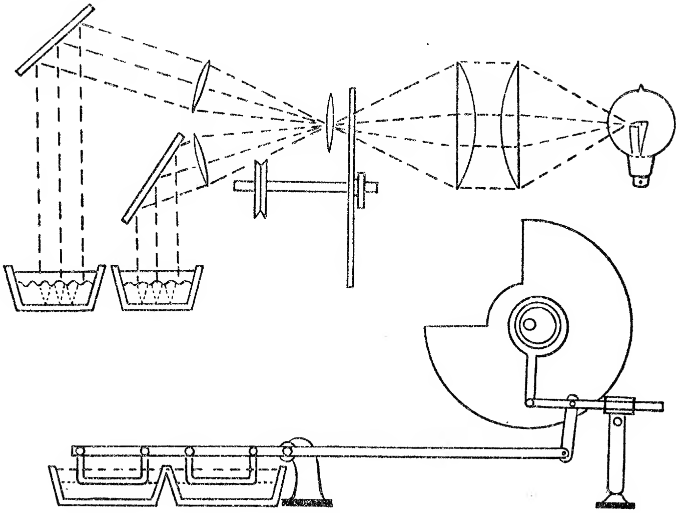

Fig. 2.

Preliminary experiments with this apparatus showed that while ripples are propagated a considerable distance when benzene forms the upper phase, even strong waves are propagated only a very short distance when pure olein forms the upper liquid. This is presumably due to the considerable viscosity of this oil.

A mixture of equal parts of olein and benzene was therefore tested with more satisfactory results. Even with this mixture, however, it is not possible to observe more than four waves at a time. Further, if the amplitude of vibration of the dipper setting up the ripples was made too great, an emulsion of the oil phase was formed in the aqueous phase. The levers which conveyed motion to the dipper from the eccentric on the motor-driven shaft were, therefore, modified so that the amplitude of vibration of the dipper could be adjusted while the apparatus was in action, the greatest amplitude being employed that did not cause emulsification. The apparatus which ran off 100-volt direct current produced approximately 2500 vibrations per minute, but the number of vibrations was not sufficiently steady to form the basis of reliable measurements. Two alternatives presented themselves: (1) to use an alternating current and a synchronous electric motor (2) to set up oscillations in two troughs side by side, and keeping one constant, to vary the conditions to be investigated in the other. The latter alternative was tried with satisfactory results and the following values obtained :—

Table IV.—Interfacial Tension by Ripple Method of 50 per cent. Olein in Benzene against Phosphate Buffered Solutions.

| $P_H$. | Vibrations per second. | $\lambda$ in cm. | $\rho$ density of oil above. | $\rho'$ density of aqueous phosphate. | Tension in dynes per sq. cm. |
|---|---|---|---|---|---|
| 4·0 | 41·4 | 0·295 | 0·90020 | 1·0808 | 13·4 |
| 7·0 | 41·4 | 0·248 | 0·90020 | 1·0598 | 8·0 |
| 8·0 | 41·4 | 0·200 | 0·90020 | 1·0458 | 4·2 |

The values in the last column were calculated from the data given in the Table according to the following formula :—

$$\text{Tension in dynes per sq. cm.} = \frac{\lambda^3\,(\text{vibs. per sec.})^2\,(\rho+\rho')}{(2\pi)} - \frac{\lambda^2 g\,(\rho'-\rho)}{(2\pi)^2}. \quad (2)$$

This formula is modified from one given by Lamb (10) and incorrectly quoted by Dorsey (8).

It will be observed that the values obtained by the ripple method are somewhat lower than those given by the drop-weight method, but it seemed to us to be outside the scope of this research to seek the cause of this difference, since the values that we obtained showed the same fall in the interfacial tension between the oil and the aqueous solution as the latter became more alkaline, that the capillary height and drop-weight methods had demonstrated. It was therefore clear that a true change in interfacial tension had been brought about and not merely a change in the so-called angle of contact.

## *Conclusion.*

Measurements of interfacial tension by the capillary-height, drop-weight and ripple methods of measuring interfacial tension agree in showing a decrease in interfacial tension between olive oil and various aqueous buffered solutions as the aqueous phase becomes more alkaline. This decrease is, at any rate in large measure, determined by the $C_H$ of the aqueous phase. In the remainder of the paper these conclusions are amplified, using the drop-weight method, which has been shown to be valid in this connection.

### Section 3.—EFFECT OF CONCENTRATION OF GLYCERIDE (OR FATTY ACID) AND ALKALI ON THE INTERFACIAL TENSION.

One of Donnan's outstanding results was that when an alkaline solution is substituted for distilled water in contact with fatty acid dissolved in benzene or petroleum, or even when associated with triglyceride, a decrease in interfacial tension is produced which is found to be a function both of the concentration of fatty substance and of the amount of alkali present.

We repeated these experiments with buffered solutions and in most respects amply proved Donnan's conclusion. For example, in the following Tables (V and VI) are given the interfacial tensions of various fatty acids and oils in benzene against acid and alkaline phosphate buffered solutions, and in two cases the effect of varying the concentration of the fatty substance in benzene is shown.

Table V.—Fatty Substances dropped through Aqueous Phase.

| Substances in benzene. | Concentration grammes of substance in 100 grm. of benzene. | Temperature. | Concentration of buffer. | Interfacial tension in dynes per cm., against | |
|---|---|---|---|---|---|
| | | | | Acid phosphate buffer $P_H$ 5·6. | Alkaline phosphate buffer $P_H$ 7·6. |
| | | ° C. | | | |
| Lauric acid*............ | 0·71 | 22·0 | Full | 29·8 | 23·1 |
| Palmitic acid*......... | 0·098 | 7·8 | ,, | 33·3 | 27·8 |
| ,, ,, *......... | 0·098 | 15·1 | $\frac{1}{3}$ | 31·9 | 28·7 |
| ,, ,, *......... | 0·098 | 28·0 | $\frac{1}{3}$ | 32·4 | 28·4 |
| Behenic acid*......... | 0·336 | 23·0 | Full | 33·1 | 26·2 |
| Oleic acid............... | 0·98 | 16·2 | ,, | 25·4 | 16·2 |
| Elaidic acid* ......... | 0·091 | 16·3 | $\frac{1}{3}$ | 31·4 | 27·7 |
| Ricinoleic acid......... | 0·1 (?) | 17·1 | $\frac{1}{2}$ | 21·0 | 13·8 |
| Palmitic acid ......... | 0·152 | 19·6 | Full | — | 29·3 |
| ,, ,, ......... | 0·076 | 20·0 | ,, | — | 30·7 |
| ,, ,, ......... | 0·0076 | 20·5 | ,, | — | 33·6 |
| ,, ,, ......... | 0·00076 | 21·0 | ,, | — | 34·4 |
| ,, ,, ......... | 0·000076 | 21·3 | ,, | — | 34·8 |
| ,, ,, ......... | zero | 20·0 | ,, | — | 34·5 |
| Triolein† .............. | 0·281 | 16·1 | Full | 29·4 | 27·7 |
| ,, †.............. | 0·499 | 16·0 | ,, | 29·2 | 27·0 |

* Pure specimens kindly supplied by Mr. N. K. Adam.

† Pure French specimen kindly supplied by Mr. Hardy.

Table VI.—Tripalmitin in benzene, 1·13 per cent. by weight.

Density taken as that of benzene borate and phosphate solutions, full buffer strength.

| Aqueous phase. | $P_H$. | Temperature in ° C. | Interfacial tension in dynes per cm. |
|---|---|---|---|
| Distilled water | — | 13·5 | 33·6 |
| Borate | 5·0 | 13·5 | 31·5 |
| Phosphate | 5·6<br>5·6 | 18·5<br>16·1 | 30·2<br>30·8 |
| | 7·4 | 15·9 | 29·6 |
| | 8·2 | 18·5 | 29·8 |
| Borate | 9·2 | 13·5 | 25·9 |
| | 10·0 | | |
| NaOH— | | | |
| N/1000 | 11·0 | 13·5 | 24·5 |
| N/20 | 12·7 | 14·0 | 17·0 |

Tripalmitin showed the first significant fall in interfacial tension at a more alkaline *p*H than triolein. We have not studied the reason for this difference from triolein, which may possibly be correlated with its higher melting point.

The above Tables V and VI show in the case of palmitic acid and of triolein in benzene the effect of changing the concentration of the fatty substance on the interfacial tension. They confirm and add to Donnan's results with stearic acid in paraffin, and to those of Harkins and Humphrey (4) for butyric acid in benzene. It will be noted, however, that, contrary to Donnan's conclusions, both triolein and tripalmitin show a lower interfacial tension for the alkaline solution than for the acid one. In the case of triolein, this is small owing to the small concentration studied.

We will now give in tabular form our results for the effect of concentration of buffered solution upon the interfacial tension.

Broadly speaking Table VII confirms Donnan's conclusions that as the concentration of the alkaline phase decreases there is a rise in interfacial tension; that is, interfacial tension increases when distilled water is replaced by the alkaline fluid. We have now to consider the effect of dilution upon the *p*H of the buffer solution. Experiments showed that in the case of phosphate solutions, dilution to 1/10th of the full strength caused a negligible change in the hydrogen-ion concentration as measured by indicators. With further dilution a change in the *p*H set in. If we confine ourselves to dilutions of alkaline buffer solutions up to 1/10th full strength, we see that oleic acid alone shows a large change in interfacial tension; so does the same acid in benzene. Triolein in benzene, on the other hand, shows some 1 per cent. variation only (within the limits of experimental error). Palmitic acid showed some 6 per cent. change. The interfacial tension for triolein therefore appeared to depend upon $p$H, whereas some other factor seemed to be concerned in the case of oleic acid.

Table VII.—Fatty Substance dropped through Aqueous Phase.

| Substance. | Concentration of substance grammes per cent. | Temperature. | Concentration of buffer. | Interfacial tension in dynes per cm., against | |
|---|---|---|---|---|---|
| | | | | Acid phosphate buffer original $P_H$ 5·6. | Alkaline phosphate buffer $P_H$ 7·6. |
| | | ° C. | | | |
| Oleic acid .............. | 100 | 16·0 | Full | 12·7 | 1·4 |
| | | | 0·5 | 13·7 | 4·8 |
| | | | 0·4 | — | 6·3 |
| | | | 0·25 | — | 8·8 |
| | | | 0·17 | — | 11·1 |
| | | | 0·1 | 13·9 | 12·8 |
| | | | 0 | 12·7 | 12·7 |
| Palmitic acid in benzene | 0·098 | 18·0 (?) | Full | 33·3 | 27·8 |
| | | 16·6 | 0·5 | — | 27·7 |
| | | 18·2 | 0·1 | 32·3 | 29·1 |
| | | 18·7 | 0·01 | — | 31·9 |
| Oleic acid in benzene | 0·983 | 16·0 | Full | 25·4 | 16·2 |
| | | 16·0 | 0·5 | 24·7 | 16·9 |
| | | 16·0 | 0·25 | 24·9 | 18·2 |
| | | 16·0 | 0·1 | 24·5 | 19·4 |
| Triolein in benzene... | 0·499 | 16·0 | 1·0 | 29·2 | 27·0 |
| | | 16·2 | 0·5 | 28·7 | 27·0 |
| | | 16·0 | 0·1 | 28·7 | 27·4 |

Table VIII brings out another difference in the behaviour of fatty acids and oils, for whereas the latter show the same interfacial tension for phosphate and borate solutions of the same $P_H$ the fatty acids or solutions of them do not.

This Table not only illustrates the different behaviour of oleic acid and olein to phosphate and borate buffered solutions, but it also shows their differences to weak unbuffered soda solutions. The situation may be summed up by the statement that whereas the oleic acid interface is "protected" against unbuffered soda solutions, it is at the same time abnormally "exposed" to the decrease in interfacial tension produced by buffered phosphate solutions. An explanation will now be given for these apparently contradictory properties.

Table VIII.—Aqueous Phase dropped into Oil.

| Substance. | Concentration (per cent.). | Temperature. | Concentration of buffer. | Interfacial tension in grammes per cm., against | | |
|---|---|---|---|---|---|---|
| | | | | Phosphate buffer $\mathrm{P_H}$ 7·6. | Borate buffer $\mathrm{P_H}$ 7·6. | NaOH N/100. |
| | | ° C. | | | | |
| Olein ............ | 100 | 15 | ½ | 7·4 | 7·2 | Unmeasurable. |
| Olein in benzene | 50 | 15 | ½ | 7·7 | 7·7 | Unmeasurable. |
| Oleic acid A...... | *100 | — | 1 | 1·4 | 16·4 | 11·0 |
| Oleic acid B...... | †100 | — | ½ | 10·8 | 17·8 | |
| Oleic acid A in benzene | 98 | 20·4 | 1 | 16·2 | 15·4 | 13·8 |
| Oleic acid B in Olein | 20 | 15 | ½ | 2·9 | 5·8 | 5·5 |

* Oleic acid A was a Kahlbaum's specimen—it was found to be very acid. Water shaken with it was found to be acid to brom-cresol blue (below $\mathrm{P_H}$ 4·6 about).

† Oleic acid B was a "pure specimen" kindly supplied by Mr. W. B. Hardy. It was found to be acid to brom-cresol purple (below $\mathrm{P_H}$ 5·6 about).

## *Cause of Discrepancy between Behaviour of Oleic Acid against Borate and Phosphate Buffer Solutions of the same* $\mathrm{P_H}$.

During the course of experiments performed to ascertain the cause of the behaviour of oleic acid to phosphate and borate buffer solutions of the same $\mathrm{P_H}$, the observation was made that when oleic acid is in contact with an alkaline fluid, there is a neutralisation of base near the interface such as does not occur if olein is used instead. Thus if a suitable indicator be added to the aqueous liquid, the change in reaction towards acid can be watched taking place near the interface. (In the case of weak ammonia solutions, neutral olein brings about a similar change.) This disappearance of base is also shown by a change in interfacial tension; for if the drop is caused to form and fall rapidly a small drop breaks away, showing a low interfacial tension; if, on the other hand, the drop is caused to form slowly a larger one breaks away, showing that the interfacial tension is now higher owing to the disappearance of base from the interface. Thus N/100 soda gave with neutral olein an immeasurably small drop, demonstrating the low interfacial tension that would be expected for a fluid so strongly alkaline. This same solution gave with oleic acid quite large drops (0·04 c.c.) showing the disappearance of base from the interface and a consequent rise in the hydrogen-ion concentration and interfacial tension. This disappearance of base and consequent production of a high interfacial tension could not have been due to the oleic acid itself. For if base had combined with the oleic acid, soap would have been formed. This, far from raising the interfacial tension, is known to lower it. The effect must, therefore, have been due to other acid substances associated with the oleic acid. Now, all samples of oleic acid tested by us were acid to litmus; it is stated that pure oleic acid should be neutral (11); our samples must, therefore, have contained acid impurities. It is known that quite simple acids, even such as acetic and formic acids, are formed in oleic acid upon standing, owing to absorption of oxygen (this is why samples of oleic acid tend to become rancid). It seems reasonable to conclude that our samples contained such acid impurities of low molecular weight. These would form simple salts readily diffusible into the body of the aqueous phase.

Three pieces of evidence can be advanced in confirmation of this view.

(1) That whereas pure oleic acid should be neutral to litmus paper, all the samples we had used gave a full acid reaction. Further, distilled water shaken with them was found to be acid to brom-cresol purple, *i.e.*, was below $P_H$ 5·6.

(2) That thoroughly washing our oleic acid with water not only made it nearly neutral to litmus, but also caused it to behave more like neutral olein.

(3) That the addition of acetic acid to olein causes it to behave as we had found oleic acid to do.

These statements are supported by the values given in Table IX.

Table IX.—Aqueous Phase dropped into Oil.

| | Interfacial tension in dynes per cm. between | | Difference in interfacial tension. |
|---|---|---|---|
| | Phosphate buffered solution $P_H$ 7·6. | Borate buffered solution $P_H$ 7·6. | |
| Neutral olein | 7·4 | 7·2 | +0·2 |
| Olein† acetic acid 0·1 per cent. | 6·7 | 9·4 | −2·7 |
| Oleic acid in benzene* | 6·25 | 7·5 | −1·25 |
| Oleic acid in benzene† | 5·33 | 5·38 | Within experimental error. |

* Acid to litmus.
† Nearly neutral to litmus.

The conclusion to be drawn from the above figures is that, if either olive oil or oleic acid, in which foreign acids are present, are brought into contact with buffered aqueous fluids, then if those fluids contain a low concentration of sodium ions (*e.g.*, borate buffers) a considerable rise in the hydrogen-ion concentration of the aqueous phase will occur at the interface, with a corresponding rise in the interfacial tension. Whereas if those aqueous fluids contain a high concentration of sodium ions (*e.g.*, phosphate buffers) only a slight rise in the H-ion concentration of the aqueous phase will occur at the interface, and therefore the rise in interfacial tension will be only a small one.

This conclusion fits in with the data at our disposal, and fully accounts for the difference in the behaviour of olein and oleic acid to buffered fluids. This explanation also covers the differences in their behaviour to unbuffered alkaline fluids, which are shown in Table X.

Table X.—Aqueous Phase dropped into Oil.

| Against. | Purified olein. | Purified olein* 5 per cent. oleic acid. | Purified olein* 20 per cent. oleic acid. | Oleic acid. | Olein* 0·2 per cent. acetic. |
|---|---|---|---|---|---|
| Distilled water ......... | 19·4 | 20·3 | 18·3 | 22·2 | 17·9 |
| N/1000 NaOH............ | 12·0 | 11·9 | 15·7 | 22·0 | 17·5 |
| N/100 NaOH ............ | 0 | 0 | 5·2 | 11·1 | 3·2 |
| Specific gravity ......... | 0·917 | 0·910 | 0·896 | 0·808 | 0·916 |
| Reaction to litmus ...... | Neutral | Neutral | Slightly acid | Acid | Acid. |

* Approximately.

The effect of the foreign acid in raising the interfacial tension is well seen in the case of N/100 NaOH. Whereas pure olein, or that to which 0·5 per cent. oleic acid had been added, gave an unmeasurably small tension; that containing 20 per cent. oleic acid, or 0·2 per cent. acetic, gave measurable tensions of 5·2 and 3·2 respectively. Further increase in either acid was found to raise the tension still further. We need hardly point out that, according to Donnan, purified olein should show no change of interfacial tension with increase of concentration of alkali, whereas oleic acid should show a large change, *i.e.*, the precise converse to the results shown in the above Table.

The practical conclusion to be drawn from the above experiments is that, when a pure triglyceride such as olein is brought into contact with different buffered fluids of the same $P_H$, the same interfacial tension is developed. If, however, oleic acid is present, then its liability to go rancid and become acid to litmus renders the interfacial tension values unreliable.

### *Behaviour of Purified Olive Oil against* N/1000 NaOH.

With regard to the discrepancy between our results and those of Donnan for the interfacial tension of purified olive oil against N/1000 soda, which led him to the view that oils only interact with bases to cause a fall in interfacial tension when they contain fatty acids as an impurity, we must admit the failure of all our attempts to prepare an oil which did not give a fall in interfacial tension when N/1000 NaOH was substituted for distilled water. Thus, a washed sample of pure olive oil gave a 50 per cent. decrease, and was found by titration to contain 3 per cent. oleic acid. The chemically equivalent amount of baryta was added and the neutral oil again tested; this also gave a 50 per cent. decrease in interfacial tension when N/1000 NaOH was substituted for distilled water. Lastly, this neutral oil was neutralised to phenol red with baryta in dilute alcohol, and removed by extraction with ether. On titration, this sample showed acids to be practically quite absent. Yet substantially the same decrease of 50 per cent. was found in the interfacial tension. We cannot, therefore, explain the discrepancy between our results and Donnan's, although we spared no pains in order to do so. It would seem, therefore, that some other explanation must be advanced for Donnan's result than the one that he gives. We have discovered incidentally that our specimens of olive oil behave in a similar way to Donnan's purified specimens when they have been saturated with $CO_2$ gas.

### *Summary of Section* 3.

From the results of this section, we conclude that the decrease in interfacial tension between fatty substances in benzene solution and aqueous buffer solutions, depends in part upon: (*a*) the concentrations of fatty substance; (*b*) the hydrogen-ion concentration of the aqueous phase.

An apparent exception to this was found in the case of oleic acid, which showed a greater decrease of interfacial tension against a phosphate buffer solution than against a borate buffer solution of the same *p*H. Evidence is brought forward in support of the view that this was caused by the presence of acid impurities in the oleic acid.

Donnan's results for the interfacial tension of purified olive oil against N/1000 soda could not be confirmed.

In the next section, consideration is given to the question of whether other chemical groups than those studied show interfacial tension differences dependent upon hydrogen-ion concentration.

## Section 4.—Relation between Chemical Constitution and Change of Interfacial Tension upon Passing from an Acid to an Alkaline Buffered Solution.

Table XI gives the interfacial tensions (and the densities used in the calculation) of a number of pure substances against acid and alkaline buffered phosphate solutions. Care has been taken to make the readings as comparable as possible.

Table XI.—Substance dropped through Aqueous Phase.

| Substances.* | Concentration of buffer. | Density. | Temperature. | Interfacial tension in dynes per sq. cm., against an | |
|---|---|---|---|---|---|
| | | | | Acid buffered phosphate solution $P_H$ 5·6. | Alkaline buffered phosphate solution $P_H$ 7·4. |
| | | | ° C. | | |
| (1) Benzene ......... | 1 | 0·8787 | 20·2 | 33·4 | 33·4 |
| (2) Toluene ......... | 1 | 0·8680 | 18·2 | 34·3 | 34·4 |
| (3) Octane ............ | 1 | 0·7060 | 17·5 | 44·6 | 43·7 |
| (4) Octylene ......... | $\frac{1}{3}$ | 0·7226 | 16·7 | 23·1 | 23·9 |
| (5) Caprylic acid ... | $\frac{1}{3}$ | 0·9118 | 17·0 | 7·31 | 6·54 |
| (6) Octyl alcohol ... | 1 | 0·8290 | 16·3 | 8·69 | 8·76 |
| (7) Hexane ............ | $\frac{1}{3}$ | 0·6601 | 18·0 | 50·97 | 49·33 |
| (8) Cyclohexane ... | $\frac{1}{3}$ | 0·779 | 16·3 | 44·75 | 45·74 |
| (9) Cyclohexanol ... | $\frac{1}{3}$ | 0·946 | 18·0 | 3·81 | 3·85 |
| (10) Oleic acid ......... | 1 | 0·898 | 16·1 | 12·6 | 1·45 |
| (11) Ricinoleic ......... | $\frac{1}{3}$ | 0·9538 | 17·0 | 6·85 | 4·41 |
| (12) Triolein ......... | — | 0·915 | 16·3 | 20·4 | 12·1 |

*Note.*—The same tip was used throughout the experiments of Tables V, VI, VII, XI.
* Pure specimens supplied by Mr. Hardy.

Interfacial tension is seen to depend upon two factors: firstly, chemical constitution, this factor causes the difference between the interfacial tension of such bodies as octane (45), and octyl alcohol (8), previously described by Hardy (12); secondly, in certain cases only, upon the reaction of the aqueous phase.

Harkins, Davies, and Clark (13) have shown that the interfacial tension between purified benzene, or toluene and water, is not affected by the reaction of the latter. Table XI shows this to be true (between the limits of *p*H investigated) of all the substances tried, with the exception of fatty acids and triolein; we have previously shown that tripalmitin in benzene solution behaves similarly. The only substances, therefore, showing change of interfacial tension with change of *p*H, are those which contain the chemically reactive ionisable group —COOH, free or in combination with glycerine.

## Section 5.—EXPLANATION OF THE FALL IN INTERFACIAL TENSION BETWEEN OILS AND ALKALINE AQUEOUS FLUIDS.

In the preceding sections we have shown that interfacial tension depends upon *p*H when a fatty acid, or triglyceride, is present at the interface. This is clearly not the only factor which can affect interfacial tension. For instance, Clowes showed, in the paper previously referred to, that the relative proportion of Na and Ca in the aqueous phase would profoundly affect interfacial conditions. We have also found that the interfacial tension of oleic acid against distilled water of varying reaction (produced by traces of $CO_2$) does not vary. It therefore appears that a small amount of alkaline substance is needed to produce the effects studied.

We have come to the conclusion that the following extension of current views correlates the facts in an orderly manner.

The fall in interfacial tension, which occurs when distilled water in contact with an oil, or fatty acid, is replaced by an alkaline fluid, is due actually to the interfacial formation of soap (salt of fatty acids). Further, the amount of this soap present interfacially, under any given set of circumstances, is determined by the reaction of the aqueous phase.

The following summarised evidence is in agreement with the view:—

(A) That the condition required for a fall in interfacial tension is that there must be in the system both a base (such as Na, K, or $NH_3$) and a fatty acid or oil.

| Phase. | I.T. |
|---|---|
| Thus 1 Benzene—NaOH .......................................... | High. |
| 2 Benzene + $NH_3$ water.......................................... | " |
| 3 Benzene—oleic acid in water .................................... | " |
| 4 Olein—water .................................................... | " |
| 5 Oleic acid......water .......................................... | " |
| 6 Olein............NaOH solution ................................. | Low. |
| 7 Olein............$NH_3$ solution ............................... | " |
| 8 Olein............$Na_2CO_3$ or borate phosphate, etc. ............ | " |
| 9 Benzene ......Na oleate........................................ | " |
| 10 Na oleate in olein water...................................... | " |
| 11 Benzene + $NH_3$......Oleic acid in water ..................... | " |

(It should be pointed out that the solution of oleic acid in water was obtained by dissolving 1 c.c. oleic acid in 1 c.c. alcohol and adding to 8 c.c. water, and filtering.)

(B) That even when both fatty acid or oil and base are present, the interfacial tension remains high if either of the chemically reactive phases cannot reach the interface owing to the formation of a more stable or less soluble compound elsewhere.

Thus 12 Olein ............ Na Cl solution ......... I.T. high.
But 13 Olein ............ Na Benzoate solution ... I.T. low.
14 Olein ............ $NH_4OH$ .................. I.T. low.

So also

15 Olein .................. $NaOH + CaCl_2$........... I.T. high.

because calcium oleate is not readily dispersed in water (see Clowes).

Similarly,

16 Lead Oleate in Benzene ... NaOH ............ I.T. high.

But remove lead by changing it to the sulphide, and I.T. immediately falls thus—

17 Lead Oleate in Benzene ... $NaOH + Na_2S$ ... I.T. low.

(C) That even if a soap is present and is able to reach the interface, the interfacial tension does not fall if a substance producing elsewhere a more stable or less soluble compound with the soap be present.

Thus 18 Benzene ............ Na Oleate solution......... I.T. low.
But 19 Benzene + 2 per cent. HA Na Oleate solution I.T. high.

Similarly,

20 Na Oleate in Olein — HCl ........................ I.T. high.

The above experiments seem to us to establish the view that the fall in interfacial tension is brought about when both base and fatty acid (or glyceride) are able to interact near the interface. Provided that enough base be present, the reaction of the aqueous phase determines how much soap will be formed in the interface. The interfacial tension is determined by the amount of such soap formed.

### *Discussion.*

(*a*) Though we have confined ourselves to a comparatively narrow range of reaction, it seems clear that hydrogen-ion concentration plays a large part in the type of interfacial change which we have been studying. There seem to be reasonable grounds for thinking that at the interface the $-COOH$ groups of fatty acids are oriented towards the water (Hardy (12), Langmuir (14), Harkins (13), Adam (15)). The effect of $P_H$ is therefore operative upon the oriented $-COOH$ group, an ionisable group, or in Hardy's terms, a group permitting of the "opening up of internal molecular fields." Associated with this, we have the fact (Langmuir and Adam) that a fatty acid occupies a 16 per cent. larger area upon the surface of acid solutions than upon alkaline ones. A transition from one volume to another occurs abruptly at about $P_H = 5 \cdot 0$. It is tempting to think that this is in some way associated with the ionisation of the $-COOH$ group. The gradual change in interfacial tension which occurs as the aqueous phase becomes more alkaline quite probably results in a gradual substitution of Na for H in COOH (*i.e.*, the formation of Na oleate at the interface) with a consequent change in interfacial tension. But considerable further experimentation is needed both to prove this and to determine the nature of the gradual change in the structure of the interface as the reaction of the aqueous phase becomes more alkaline. This change in the case of the fatty acid eventually resolves itself into complete aqueous solution as a soap at a $P_H$ of $8 \cdot 0$ approximately. A correlation of these facts with problems of the iso-electric point of amphoteric and protein-like substances would be of interest.

(*b*) In a consideration of the mechanism by which change in $P_H$ of the aqueous phase produces effects upon the $-COOH$ group at the interface, it is well to remember that Haber and Klemensiewicz (16) showed that, in the case of the benzene-water system, there may be differences of potential of as much as 1 volt produced at the interface by a small change of concentration from base to acid near the neutral point. This electrical change is likely to be an expression of a re-orientation of water molecules at the interface. In the absence of a reactive group it may be that these electrical changes appear instead of changes in interfacial tension.

We feel that the view that we have put forward explains some of the effects observed by Shorter and Ellingworth (17). These observers found that the addition of alkali to soap solutions decreased the observed interfacial tension between these solutions and benzene. This is correlated with the well known effect of alkalies in assisting the emulsifying action of soap solutions. In our view, the effect of the added alkali is due to the decrease in the H-ion concentration of the solution.

One physiological application requires comment. Harkins, Davies, and Clark concluded from their experiments upon the benzene-water interface, that the changes in interfacial tension produced by acid and alkali were not sufficient to account for muscular motion. In criticism, it must be pointed out that, theoretically, all that is needed to obtain the necessary type of interfacial change is a series of $-COOH$ groups arranged so that they can react to changes of hydrogen-ion concentration. Such $-COOH$ groups might well be part of the protein structure of the contractile mechanism of the muscle. Whether changes of a sufficient order of magnitude could be produced would depend largely upon the dimensions and structure of the system.

## *Summary.*

1. A comparison of the capillary height, drop-weight, and a modified ripple method of measuring interfacial tension, shows that the drop-weight method is valid for comparing the interfacial tensions of oils, or fatty acids, against aqueous solutions of varying reactions.

2. Using the drop-weight method the following observations have been made:—

The decrease in interfacial tension between fatty substances in benzene solution and aqueous " buffered " solutions depends upon—

(*a*) The concentration of fatty substance.

(*b*) The presence of a small amount of "available" monovalent alkali in the aqueous phase, *i.e.*, alkali not in combination with strong acid.

(*c*) The hydrogen-ion concentration at the interface.

For a series of pure substances, it is found that the changes in interfacial tension produced by changes in reaction of the aqueous phase (*i.e.*, decrease in interfacial tension with increase of alkalinity) occur only with the substances which have the —COOH group, free or in combination, as glyceride.

A hypothesis is developed to correlate the above conclusions.

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